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Simultaneous determination of five common additives in insulating mineral oils by high-performance liquid chromatography with ultraviolet and coulometric detection

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Running title: Simultaneous antioxidant and passivators analysis in mineral oils

Abbreviations: ASTM, American Society for Testing and Materials; BTA, benzotriazole; DBP, 2,6-di-tert-butylphenol; DBPC, 2,6-di-tert-butyl-p-cresol; DC, direct current; $E_{p,ox}$, oxidation potential; GBC, graphitized black carbon; IEC, International Electrotechnical Commission; i_p , peak current intensity; NPN, N-phenyl-1-naphtylamine; PSA, primary secondary amine.

Keywords: antioxidants; coulometric detection; inhibitors; mineral oil; monitoring.

Abstract

25 Dielectric mineral oils are used to impregnate power transformers and large electrical apparatus,
26 acting as both liquid insulation and heat dissipation media. Antioxidants and passivators are
27 frequently added to mineral oils to enhance oxidation stability and reduce the electrostatic charging
28 tendency, respectively. Since existing standard test methods only allow analysis of individual
29 additives, new approaches are needed for the detection of mixtures.

30 For the first time we investigate and discuss the performance of analytical methods, which require
31 or do not require extraction as sample pretreatment, for the simultaneous reversed-phase HPLC
32 determination of passivators (benzotriazole, Irgamet® 39) and antioxidants (N-phenyl-1-
33 naphthylamine, 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-p-cresol), chosen for their presence in
34 marketed oils. Quick Easy, Cheap, Effective, Rugged and Safe and solid phase extractions were
35 evaluated as sample pretreatments. Direct sample-injection was also studied. Ultraviolet
36 spectrophotometry and direct-current coulometry detection were explored. As less prone to
37 additive concentrations variability, the direct-injection-HPLC-ultraviolet-coulometric detection
38 method was validated through comparison with Standard Method IEC 60666 and through an ASTM
39 inter-laboratory proficiency test. Obtained detection limits are (mg kg^{-1}): benzotriazole (2.8),
40 Irgamet® 39 (13.8), N-phenyl-1-naphthylamine (11.9), 2,6-di-tert-butylphenol (13.1), 2,6-di-tert-
41 butyl-p-cresol (10.2). Simultaneous determination of selected additives was possible both in unused
42 and used oils, with good precision and accuracy.

43

44 **1 Introduction**

45 The performance and stability of insulating mineral oils are improved by the addition of additives
46 such as antioxidants (inhibitors) and corrosion inhibitors, more widely known in the electrical
47 industry setting as passivators [1].

48 Antioxidants can be classified as primary antioxidants (radical scavengers, often known as inhibitors)
49 and secondary antioxidants (easily oxidable molecules) [2]. The formers (inhibitors) are widely used
50 in the production of the so-called inhibited insulating oils. The most widely used inhibitors belong
51 to the family of the hindered phenols: 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-p-cresol. Amine-
52 based inhibitors are not very diffused in the production of inhibited oils, due to their toxicity, but
53 are largely used in lubricating oils. Inhibitors can degrade during the oil's life, and require monitoring
54 to allow the appropriate corrective action (e.g. inhibitor restore or oil's replacement).

55 Corrosion inhibitors (passivators) are added for several purposes: to mitigate corrosion problems of
56 the copper conductors, as indirect antioxidant (they protect the metal surfaces, that promote
57 oxidation by catalysis), and to reduce the tendency of the oil to electrostatic charging [3] (especially
58 in case of rapid oil flow through small pipes, as in oil forced cooling). They are prone to degradation,
59 in the presence of thermal stress or in oils with high concentration of peroxyradicals, and they
60 require a regular monitoring to prevent their reduction below the value at which they become
61 ineffective [4].

62 The lack of analytical methods able to determine antioxidants and passivators in a unique run was
63 extensively discussed by Bruzzoniti et al. [5], where we proposed and validated a SPE-HPLC-UV
64 detection method for the simultaneous analysis of the five commonest additives found in insulating
65 mineral oils (antioxidants: DBPC, DBP, NPN; passivators: BTA, Irgamet® 39), which provided
66 apparent recoveries in the range 80-87% for BTA, Irgamet® 39 and NPN and 53% and 15% for DBP
67 and DBPC respectively.

68 An evident weak point of the above mentioned method was the low recovery yield of some the
69 compounds. Moreover, DBP and DBPC peaks tend to elute close to peaks corresponding to matrix
70 oil components, resulting in a difficult quantification of these compounds. With the aim of improving

71 these aspects, in this work we optimized a coulometric detection technique, allowing an additional
72 selective criterion besides chromatographic separation [6,7].
73 Matrix interference due to oil complexity was also coped comparing QuEChERS as sample
74 pretreatment approaches, which is employed for extraction and clean-up of selected classes of
75 pollutants from food [8] and recently from environmental [9,10] matrices. Although the technique
76 was applied for the analysis of medium polarity compounds ($\log P=4.6-6.5$) in vegetable oil samples
77 [11], to the best of our knowledge, this work represents the first investigation on QuEChERS
78 approach to insulating mineral oil analysis.
79 Finally, under the rationale that the coulometric electrochemical detection is less prone to
80 interference due to its high specificity, the direct injection of the sample was also evaluated. This
81 last approach, which was characterized by high simplicity and high analytical throughput since no
82 sample pretreatment was required, proved to be very sensitive. The method was validated and
83 applied for the analysis of both new and in service transformer oils.

84

85 **2 Materials and methods**

86 **2.1 Chemicals and materials**

87 All chemicals used were of analytical grade. BTA (>99%) from Fluka (Milan, Italy), DBPC (>99%) and
88 DBP (>98%) were from Alfa Aesar (Lancashire, UK), NPN (>99%) was from Acros Organics (Thermo
89 Fisher, Milan, Italy) and Irgamet® 39 was from Ciba-Geigy (Lumar Italia, Milan, Italy). Pentane
90 (>99%), methanol, acetonitrile, isopropanol and water (all HPLC gradient grade) were from Panreac,
91 Novachimica (Cinisello Balsamo, Milan, Italy). Sodium chloride and magnesium sulphate, ACS
92 reagent salts, were supplied by Riedel-de Haën (Seelze, Germany). End-capped C18, PSA and GBC
93 SPE bulk sorbent used for the clean-up step, were from Agilent Technologies (Santa Clara, CA, USA).

Oil samples used for the evaluation of the performance of methods are detailed in the Supporting Information section. All the uninhibited oils were preliminary analyzed in order to ascertain the absence of the five additives.

97

2.2 Instrumentation

Chromatographic analyses were performed with a HP 1050 Chemstation (Agilent, Milan, Italy) equipped with both a G1315B Agilent diode array detector and a Coulochem II (ESA, MA, USA) electrochemical detector equipped with a Model 5011 analytical cell with porous graphite working electrode (counter and reference electrode: Pd). For spectrophotometric measurements, 265 nm was set as detection wavelength, whereas the oxidation potential at channel 1 was set at 700 mV (optimized through hydrodynamic voltammetry experiments, see section 2.4 and 3.1). For Coulochem II detector, other conditions were gain range: 100 μ A; filter time: 2 s; signal output: 1 V; output offset: 0%. The column used was a Kinetex 5 μ m Phenyl-Hexyl (250 x 4.6 mm) (Phenomenex). The eluent flow rate was 1 mL/min and the injection volume was 10 μ L.

108

2.3 Elution conditions

After optimization, the best conditions for the separation of analytes were achieved by the following gradient composition: t= 0 -15 min: 50 mM acetate buffer (pH 4.76), CH₃CN from 30 to 80%; t= 15-30 min: 50 mM acetate buffer (pH 4.76), 80% CH₃CN; t=30.1-35 min: 50 mM acetate buffer (pH 4.76), 30% CH₃CN. For direct injection of oils, an additional washing step with isopropanol was introduced as further detailed in section 3.3. For Irgamet[®] 39, a peak splitting was observed throughout the work. This is usually interpreted with the presence of two isomers (N,N-bis(2-ethylhexyl)-4-methyl-1H-benzotriazole-1-methamine and (N,N-bis(2-ethylhexyl)-5-methyl-1H-benzotriazole-1-methamine) present in Irgamet[®] 39 which are not baseline resolved [12].

118 Nevertheless, under elution conditions, hydrolysis of Irgamet® 39 to tolyltriazole *via* retro-Mannich
119 reaction was observed [13] and therefore Irgamet® 39 is most likely revealed as 3-N-methyl-6-
120 methyl benzotriazole and 3-N-methyl-7-methyl benzotriazole. Of course, the calibration done with
121 Irgamet®39 ensures the correct quantitative detection, notwithstanding the reaction of the
122 molecules during the analysis.

123

124 **2.4 Hydrodynamic voltammetry**

125 To generate the current/voltage curve for the selected analytes, a mixture of BTA, Irgamet® 39,
126 NPN, DBP and DBPC was prepared at 50 mg kg⁻¹ each. The mixture was injected and eluted by mobile
127 phases buffered at three different pH values: (i) 0.05 M HCOOH/HCOONa pH 2.8; (ii) 0.05 M
128 CH₃COOH/ CH₃COONa pH 4.8; (iii) 0.05 M H₃PO₄/Na₂HPO₄ pH 6.0. The coulometric detector was set
129 at a given potential (*E*) and the chromatogram collected. The peak area was measured for each
130 additive in the sample. The process was repeated with varying potentials until sufficient data were
131 collected and a peak area vs applied potential curve was generated. The potential was varied in the
132 range -700 mV - 1400 mV (with increasing steps of 100 mV).

133

134 **2.5 Sample treatment**

135 As above mentioned, QuEChERS, and SPE were evaluated as sample pre-treatments for the removal
136 of matrix interferences. Details on these approaches are hereafter given.

137

138 *QuEChERS extraction:*

139 10 g sample weighed in a centrifuge tube were added with 10 mL of CH₃CN, 4 g of anhydrous MgSO₄,
140 1 g NaCl and shaken for 1 min. After centrifugation (3700 rpm for 2 min) the supernatant,
141 acetonitrile phase, was transferred to a 5 mL centrifuge tube containing 250 mg of sorbent (using

142 alternatively PSA, C18, GBC or a mixture 1:1:1 of the three sorbents) together with 750 mg of MgSO₄.
143 The tube was shaken for 1 min, centrifuged for 2 min at 3700 (rpm) and finally the supernatant was
144 diluted 1:5 and analyzed by HPLC.

145

146 *SPE extraction:*

147 0.5 g samples in 2.5 mL pentane were loaded through 500 mg silica cartridges (Sep-Pak Plus,
148 Waters) pre-activated with 5 mL pentane. The cartridge was dried under vacuum (20 min) and the
149 additives were recovered with 5 mL 40:60 (% v/v) H₂O:CH₃CN and analyzed by HPLC.

150

151 **3 Results and Discussion**

152 **3.1 Optimization of electrochemical detection**

153 A wide variety of compounds are capable of being monitored by electrochemical detection at
154 porous carbon electrode. The surface area of the electrode inside the cell is very large, so that all of
155 the electroactive species is oxidized without a corresponding increase in noise, thus providing
156 enhanced sensitivity. Many compounds which are easily oxidized contain groups with lone pair of
157 electrons such as the hydroxyl or the amino groups. In order to set proper oxidation potential for
158 the chromatographic detection, hydrodynamic voltammetry was used to generate peak
159 area/voltage curves. The curves, which were generated by three buffers at three different pH values
160 (2.8, 4.8 and 6.0), are shown in Figure S1 of Supporting Information section. It should be noted that
161 the observed current does not include a contribution from capacitive effects since the potential is
162 allowed to equilibrate before the current data is collected.

163 The results obtained can be hereafter summarized:

164 BTA: for this triazolic compound, low oxidation peak areas (400-500 μ A·sec) are obtained at pH 4.8
165 and 6.0 in the range $E_{p,ox}$ -0.4 to 0 V.

166 Irgamet® 39: also for this triazolic compound, a poor i_p response is obtained in the range $E_{p,ox}$ -0.4
167 to 0 V.

168 NPN, DBP and DBPC exhibited oxidation signals which were pH dependent. For these compounds,
169 oxidation occurred at lower E values for acetate, phosphate and formate buffers, respectively.

170 The possibility to detect at the lowest E value as possible is highly desirable, since background
171 current is kept to a minimum and *signal-to-noise* ratio is maximized.

172 Although the good signals obtained for formate buffer, at this pH conditions instability of the signal
173 was observed. At a given E value, oxidation currents obtained with acetate buffer are higher than
174 those obtained by phosphate buffer. Therefore, for the above mentioned reasons, the acetate
175 buffer was selected as the eluent. According to the data obtained, using this buffer, coulometric
176 detection performed at $E_{p,ox}$ 0.7 V is amenable for the detection of the NPN, DBP and DBPC, with
177 good i_p response, with low background current.

178

179 **3.2 Extraction of additives from oils**

180 Several extraction techniques of additives from oils were studied and compared as described
181 hereafter. The extracted solutions were injected in the HPLC system which was coupled with
182 spectrophotometric and coulometric detectors in series. Elution was performed by the gradient
183 conditions specified in the experimental session. Detection was performed by UV detection (265
184 nm) for BTA, Irgamet® 39 and by coulometric detection (700 mV) for NPN, DBP and DBPC.

185 The performance of extractions conditions was tested for unused and in-service oil, in order to
186 assess the effect of the aged matrix on the recovery. For each extraction procedure, recovery for
187 each compound was calculated by the use of a calibration curve obtained in the recovery solution.
188 For BTA and Irgamet® 39, recovery was calculated by peak areas obtained from UV detector,

189 whereas for NPN, DBP and DBPC, recovery was calculated by peak areas obtained from coulometric
190 detection.

191

192 **3.2.1 QuEChERS extraction**

193 The original QuEChERS approach [8] involves a liquid-liquid extraction of the sample in the presence
194 of salts followed by a dispersive solid-phase extraction (*d*-SPE) clean-up step of the extract. This
195 approach can therefore be regarded as a promising isolation method of the co-extracted matrix and
196 then enhance recovery of DBP and DBPC which elute close to matrix oil components.

197 Preliminary experiments were performed in order to evaluate the performance of PSA, C18 silica
198 and GBC in the *d*-SPE step on additive recoveries. Analytes were dissolved at 50 mg L⁻¹ into an
199 unused uninhibited oil DIALA B. Being this matrix not affected by ageing of the oil, it is free from
200 compounds typically derived from oil degradation (i.e. acids, aldehydes, ketones).

201 Extraction yields obtained (Figure S2 of Supporting Information section) show that only the
202 recoveries of BTA ($\log P_{\text{BTA}}=1.3$) and Irgamet® 39 are affected by the type of *d*-SPE sorbent. The low
203 recovery of BTA (18%) with PSA can be attributed to analyte adsorption by PSA, probably due to H-
204 bonding interactions (see comments in the Supporting Information section), even enhanced in the
205 aprotic solvent acetonitrile. For Irgamet® 39, higher steric hindrance limits the interaction and
206 slightly enhance overall recovery (26%) in respect to BTA. Higher recoveries for NPN, DBP and DBPC
207 for PSA are probably due to additives lower polarity ($\log P_{\text{NPN}}=4.4$; $\log P_{\text{DBP}}=4.8$; $\log P_{\text{DBPC}}=5.3$) and
208 steric hindrance. As regards phenolic compounds, they exhibit moderate affinity for GBC and hence
209 slightly reduced recoveries in comparison with other *d*-SPE sorbents.

210 In order to ascertain if the recoveries of DBP are affected by the extraction step or by the clean-up
211 step of the QuEChERS procedure, the procedure was repeated in the presence and in the absence
212 of the *d*-SPE step (Table1). To assess the suitability of the QuEChERS approach also with aged oils,

213 the procedure (with and without *d*-SPE) was repeated on used uninhibited oil (manufactured in
214 2001), retrieved from an in-service distribution transformer (France).

215 The *d*-SPE step chosen was based on of mixed sorbent (1:1:1, PSA:C18:GBC) in order to provide
216 multiple interaction sites for the removal of the oxidized compounds contained in the used oil. To
217 these oils, additives were spiked at concentrations typically contained in the transformer oils.

218 Unexpectedly, the performance of the QuEChERS extraction is not matrix dependent, since
219 comparable recoveries are obtained for both unused and in-service oils. Additionally, the low
220 recoveries obtained for phenolic and cresol compounds are not ascribed to any adsorption onto the
221 *d*-SPE sorbent, but to a fair extraction in CH₃CN. The adsorption of BTA and Irgamet® 39 onto PSA is
222 confirmed by the decreased recovery obtained in the presence of the *d*-SPE step. Although the *d*-
223 SPE provided a clearer extract for used oil, this improvement is not observed in the UV baseline of
224 the chromatograms.

225 Figure 1 clearly shows that the use of the electrochemical detector removes baseline interferences
226 due to non-polar compounds on the detection of phenolic additives, and therefore this detection
227 approach is advisable for the monitoring of aged oils. Less critical is the analysis of additives in
228 unused oils (Figure S3 of Supporting Information section), even if better *signal-to-noise* ratio are
229 obtained for coulometric detection.

230 Recovery of all analytes in the liquid-liquid extraction step of the QuEChERS approach was studied
231 as a function of initial concentration of additives in oil for reliable monitoring of oil. To accomplish
232 this task, six DIALA B aliquots samples were spiked in triplicate with BTA (ranging from 5-48 mg kg⁻¹),
233 Irgamet® 39 (37-187 mg kg⁻¹), NPN (220-723 mg kg⁻¹), DBP (114-3993 mg kg⁻¹), and DBPC (104-3923
234 mg kg⁻¹), and analyzed. The recovery data obtained (% , n = 3) were: BTA (51-89), Irgamet® 39 (40-
235 68), NPN (80-87), DBP (25-30), and DBPC (22-30), and indicated a dependence of recovery values
236 for analytes upon concentration. Overall better results in terms of recovery can be obtained by

237 increasing the solvent/sample ratio (5:1 v/w) interpreted as a better contact between oil and
238 acetonitrile, but these values are still affected by initial concentration. Experimental results
239 obtained for the extraction of additives from DIALA B at 1:1 and 5:1 (v/w) solvent:sample ratio, for
240 single additive or mixtures are reported in Figure S4 and S5 of Supporting Information section,
241 where a strong dependence of recovery values for DBPC (45-95%) upon concentration is highlighted.

242

243 **3.2.2 Solid phase extraction**

244 SPE is recommended by IEC 60666 [14] for the analysis of Irgamet® 39. We here investigate the
245 effect of the initial concentration of additives in oil on recovery. Experiments were performed on
246 unused oil (DIALA B) in order to have recovery values not biased from the aged oil matrix. DIALA B
247 was spiked with the additives in the following ranges (mg kg⁻¹) which are representative of real case-
248 in service oils: 5-50 BTA, 37-190 Irgamet® 39, 220-720 NPN, 100-4000 DBP, 100-4000 DBPC.
249 Recovery yields (%) were evaluated in triplicate, and the following ranges were obtained: BTA (98-
250 100), Irgamet® 39 (99-100), NPN (88-99), DBP (81-95) and DBPC (65-88), see Figure S6 of Supporting
251 Information section. As shown, extraction for DBP and DBPC exhibits an overall lower efficiency
252 which is also dependent on initial concentration.

253 Worth mentioning that only the use of coulometric detection allows to obtain reliable identification
254 of DBPC peak for the lowest concentration values (see Figure S7 of Supporting Information section).
255 Major baseline interference should be expected for aged oils in case of UV detection [5].

256

257 **3.3 Direct injection**

258 On the basis of the good performance obtained with coulometric detection, we tested direct-
259 injection coupled to HPLC-UV-coulometric detection as a new approach for the analysis of additives
260 in oils. Direct injection of oils carries out evident disadvantages such as saturation of the column. In

fact, after seven consecutive injections of mixtures of an unused oil (Hyvolt I) spiked with 50 mg kg⁻¹ of each additive, broad peaks are obtained for BTA, Irgamet® 39 and NPN and shift of retention times for all additives.

To avoid column saturation, a 15 min-long washing step with isopropanol was added, modifying the eluent into t= 0 -23 min: 50 mM acetate buffer (pH 4.76), CH₃CN from 30 to 80%; t= 23-38 min 100% isopropanol (flow rate 0.5 mL/min); t=38.1-43 min: 50 mM acetate buffer (pH 4.76), 30% CH₃CN. During the washing step with isopropanol, the flow rate (1 mL/min) was reduced in order to avoid increased column backpressure.

Since direct injection method looks the most promising among the approaches tested, figures of merits were determined. The presence of any matrix effect (ME) was initially investigated by comparing the peak areas obtained after injection of standard solutions prepared in acetonitrile (A_{std,CH₃CN}) with those obtained by standard solutions prepared in unused oil (A_{std,oil}) according to the expression:

$$ME=100 * (A_{std,oil} - A_{std,CH_3CN}) / A_{std,CH_3CN}$$

The matrix effects determined by UV detection for BTA and Irgamet® 39 and by coulometry for the others were: BTA -9%, Irgamet® 39 -2%, NPN -10%, DBP +7% and DBPC+33%. For BTA and Irgamet® 39, the lack of signal enhancement in the spiked oil, compared to standard in solvent, is in agreement with the absence of significant co-elutions among target analytes and matrix components, which represents the only important source of the positive matrix effect with UV detection. For the coulometric detection, a significant effect of the oil matrix was observed for DBPC. According to the results obtained, matrix-matched calibration was used, spiking Hyvolt I with mixtures of the five additives at n=5 levels representing concentrations actually used in commercial oils. Linearity ranges were 10-50 mg kg⁻¹ for BTA, 50-200 mg kg⁻¹ for Irgamet® 39, 40-200 mg kg⁻¹ for NPN, 40-1000 mg kg⁻¹ for DBP and 30-200 mg kg⁻¹ for DBPC. For higher concentrations of DBP

285 and DBPC, dilution in isopropanol is recommended to keep linearity of the calibration curve.
286 Equations and R^2 obtained are reported in Table S1 of Supporting Information. Detection and
287 quantification limits (mg kg^{-1}), evaluated according to the ICH guidelines [15] were: BTA (2.8 - 8.6),
288 Irgamet® 39 (13.8-41.8), NPN (11.9 - 36.1), DBP (13.1 -40.0), DBPC (10.2 - 30.8) and satisfy the
289 analytical requirements in respect to the concentrations usually employed and the depletion
290 concentration for which maintenance guides suggest to restore the additives [16]. It is worth
291 mentioning that, the relative standard deviation of retention times of DBPC (monitored for a six-
292 month period of direct-injection of oil) was about 1.5%.

293

294 **3.3.1 Method validation**

295 The precision of the method was evaluated for Irgamet® 39 and DBPC since they are the most used
296 passivator and inhibitor, respectively. For the choice of samples to analyze, it should be highlighted
297 that unused oil produced in the last decade do not usually contain passivators, because such
298 additives are mainly used at least in European market to mitigate the detrimental effect of oil
299 containing corrosive sulfur [17]. After 2006, corrosive sulfur has been practically banned from
300 unused mineral insulating oils. Therefore, for the evaluation of precision for Irgamet® 39, an oil
301 sampled from an auxiliary transformer in generation plant (Italy) manufactured in 2003 was chosen.
302 Precision for DBPC was evaluated in unused DIALA DX (inhibited by manufacturers with DBPC) oil.
303 The samples were analyzed by direct in-column injection through $n=20$ replicates. Concentrations
304 obtained were $231.8 \pm 5.4 \text{ mg kg}^{-1}$ for Irgamet® 39 and $3266 \pm 120 \text{ mg kg}^{-1}$ for DBPC. Precision of the
305 direct-injection method was compared with that of Standard Method IEC 60666 (HPLC for Irgamet®
306 39 and FT-IR for DBPC) [14] through the *F-test*. The *F* parameters obtained (Irgamet® 39: 0.88 and
307 DBPC: 0.24) compared with the *F* critical value (2.17) highlights comparable precision for the two
308 methods.

309

310 **3.3.1.1. Oil analysis**

311 Unused Hyvolt II and DIALA DX and two naphthenic uninhibited mineral oils (manufactured on 2003),
312 added with Irgamet® 39, sampled from two twin auxiliary transformers installed in the same
313 generation thermal power plant (Italy) were analyzed by direct-injection and by Standard Method
314 IEC 60666 (Table 2). The deviations, calculated as difference between the values obtained by direct-
315 injection and those obtained by the Standard Method divided by the target value (assumed to be
316 the ones measured by IEC 60666), are included within the window of reproducibility accepted by
317 IEC 60666 ($\pm 22.5\%$ DBPC, $\pm 4\%$ Irgamet® 39) showing that the method is characterized by good
318 accuracy.

319 The method was tested for DBPC determination inside an ASTM Proficiency Testing Program
320 “Insulating Fluid Quality (IFQ1303)”, March 2013. Two used in-service oils containing DBPC were
321 analyzed by different laboratories according to ASTM D4768 [18] by GC and with the developed
322 method. The Z-score values obtained, 0.66 and 0.02, confirmed an excellent accuracy ($Z < 1$) of the
323 method.

324

325 **3.3.1.2. Strongly Aged Oil Analysis**

326 To verify the suitability of the method, two used (strongly aged) uninhibited oils of paraffinic type,
327 retrieved from in-service industrial distribution transformers (oils manufactured on 1974 and 1987),
328 Italy, were spiked with the five additives and analyzed by direct-injection as such or after 1:20
329 dilution, coupling UV (BTA and Irgamet® 39) and coulometric (NPN, DBP, DBPC) detection. Figure 2
330 clearly shows that the high selective coulometric detection allows for overcoming all potential
331 matrix interferences as well as for obtaining excellent additive recoveries, Table 3.

332

333 **4 Concluding remarks**

334 The surveillance of additives contained in aged oils is of outmost importance in the life-cycle
335 management of mineral insulating oils. Reliable analytical approaches to be possibly applied in
336 routine modes are needed to ensure quantification. Analytical approaches that use sample
337 pretreatment (QuEChERS and SPE) can provide cleaner extracts for aged oils, which, on the other
338 hand, are not completely free from interferences in the elution windows of DBP and DBPC, making
339 necessary the use of a selective detector. Additionally, since recoveries can be affected by initial
340 concentration of additives, a correct quantification can be therefore prevented even with standard
341 addition methods.

342 Direct injection, which does not suffer from intrinsic drawbacks of extraction methods, requires the
343 use of the selective coulometric detector. Although shorter durability of chromatographic column
344 in respect to extraction methods must be expected, the direct-injection HPLC-UV-coulometric
345 method allows for simultaneous determination of passivator and antioxidant additives both in
346 unused and strongly aged insulating oils with good precision and accuracy. In particular, deviations
347 calculated in respect to the IEC 60666 method were <5% for Irgamet® 39 and <3%. Recoveries of
348 the five additives spiked in in-service oils were included within 95 and 98.5%. Coulometric detection
349 furnished a great improvement in sensitivity for DBP and DBPC analysis [5], providing detection
350 limits of tens mg kg⁻¹.

351

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357

358 **Conflict of interest statement**

359 The authors declare no conflicts of interest.

360

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416

417 **Figure Captions**

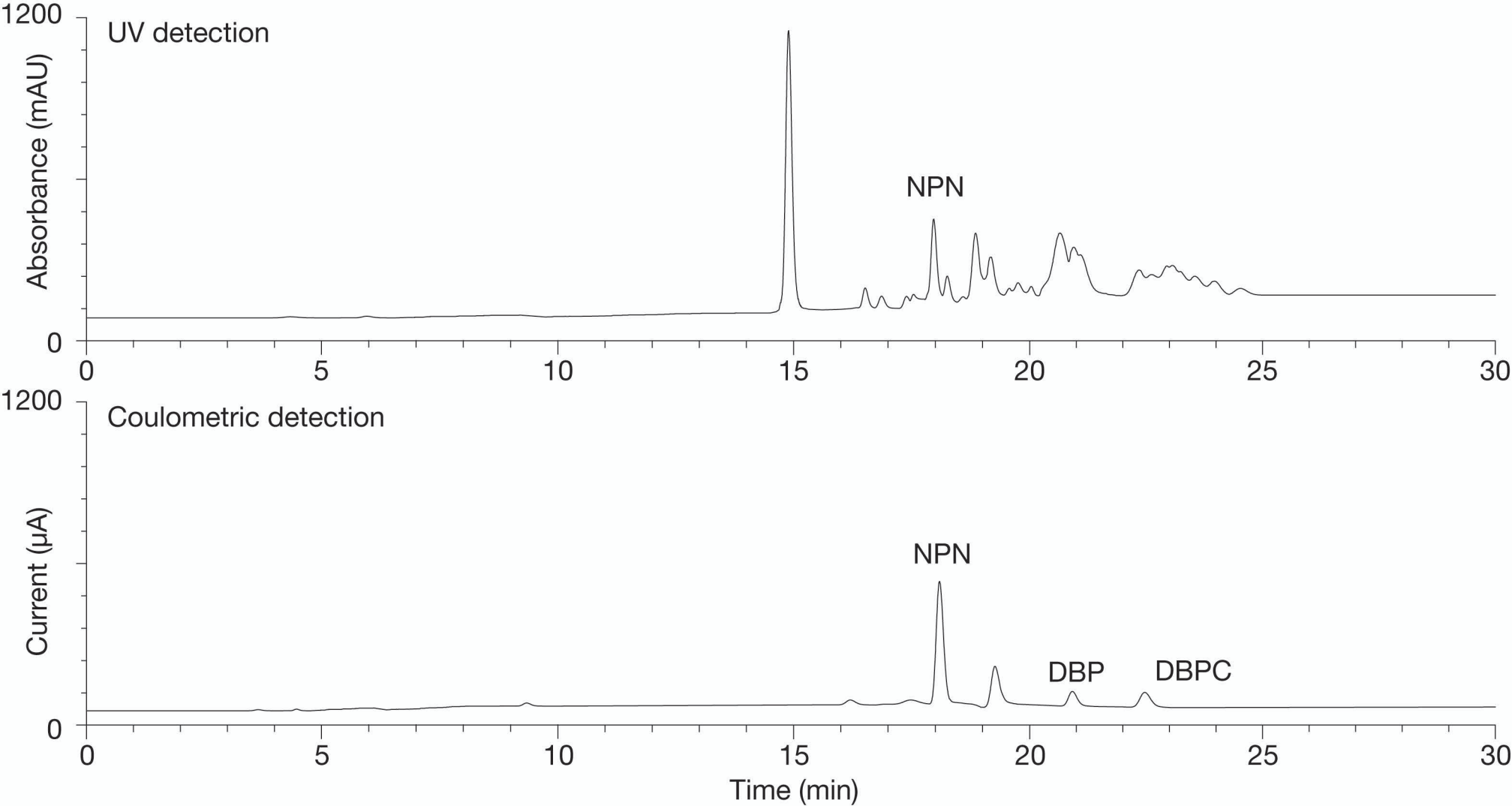
418 **Figure 1.** HPLC-UV and HPLC-coulometric analysis of used uninhibited oil (manufactured in 2001),
419 retrieved from an in-service distribution transformer in France spiked with the additives
420 (concentrations as for Table 1) after QuEChERS extraction with *d*-SPE clean up.

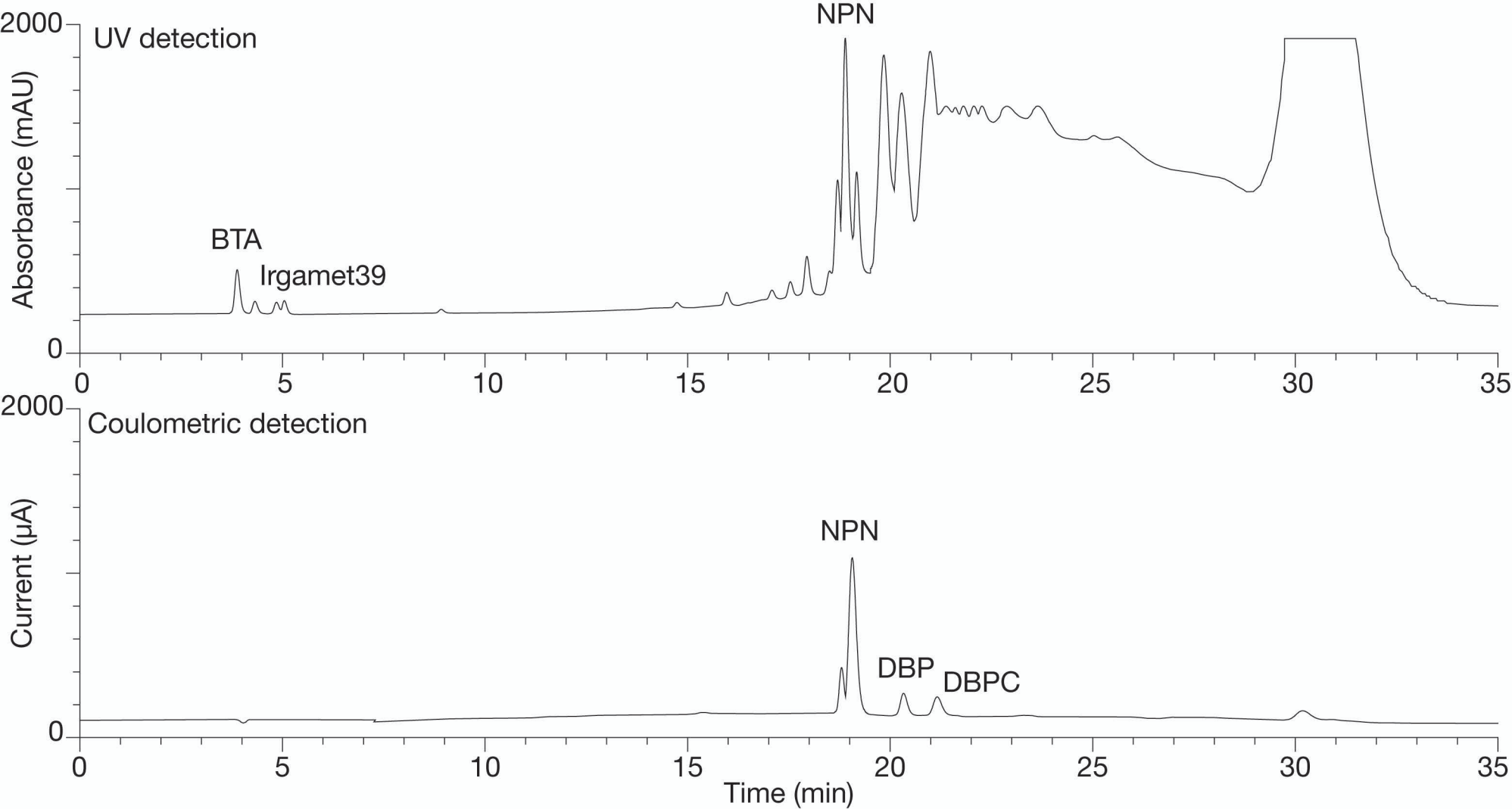
421

422 **Figure 2.** Direct injection of strongly aged uninhibited oils of paraffinic type, retrieved from in-
423 service industrial distribution transformers spiked with 52 mg kg⁻¹ BTA, 96 mg kg⁻¹ Irgamet® 39, 416
424 mg kg⁻¹ NPN, 725 mg kg⁻¹ DBP and 706 mg kg⁻¹ DBPC. (a): UV detection; (b): coulometric detection.

425

426





1 **Table 1.** Effect of *d*-SPE and matrix oil composition on recovery by QuEChERS procedure

Additive	Actual concentration (mg/kg)	Recovery (%)			
		DIALA B ^{a)}	Used oil ^{a)}	DIALA B ^{b)}	Used oil ^{b)}
<i>BTA</i>	30	58.6	54.0	34.3	38.1
<i>Irgamet®39</i>	97	53.3	55.7	33.2	41.3
<i>NPN</i>	500	78.7	80.1	80.5	80.8
<i>DBP</i>	2000	18.2	17.8	19.6	19.1
<i>DBPC</i>	2000	19.8	23.4	20.9	20.3

2 ^{a)} without *d*-SPE.

3 ^{b)} with *d*-SPE.

1 **Table 2.** Analysis of Irgamet® 39 and DBPC in used and unused oils by this method and the IEC 60666 method
2 (HPLC for Irgamet® 39 and FT-IR for DBPC)

Additive (oil)	Direct-injection (mg/kg)	IEC 60666 (mg/kg)	Deviation (%)
Irgamet® 39 (in service oil ^{b)})	202	195	3.5
Irgamet® 39 (in service oil ^{b)})	243	254	-4.4
DBPC (Hyvolt II)	2769	2700	2.6
DBPC (DIALA DX)	3349	3300	1.5

3 ^{a)} Naphtenic uninhibited mineral oils from auxiliary transformers (2003, thermal generation power plant, Italy).

4

1 **Table 3.** Analysis of two aged oils spiked with known amounts of additives by HPLC-UV-coulometric detection

Additive	Aged oil #1 ^{a)}			Aged oil #2 ^{b)}		
	Spike (mg/kg)	Measured (mg/kg)	Deviation (%)	Spike (mg/kg)	Measured (mg/kg)	Deviation (%)
BTA	49.9	47.8	-4.3	52	49	-5.0
Irgamet® 39	129	124	-3.9	96	95	-1.5
NPN	465	444	-4.5	416	410	-1.4
DBP	742	753	1.6	725	748	3.2
DBPC	708	725	2.4	706	741	4.9

2 ^{a)} manufactured in 1974.

3 ^{b)} manufactured in 1987.